

# Organization of atomic bond tensions in model glasses

T. Kustanovich and Y. Rabin

*Department of Physics, Bar Ilan University, Ramat-Gan 52900*

Z. Olami

*Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel*

In order to understand whether internal stresses in glasses are correlated or randomly distributed, we study the organization of atomic bond tensions (normal forces between pairs of atoms). Measurements of the invariants of the atomic bond tension tensor in simulated 2D and 3D binary Lennard-Jones glasses, reveal new and unexpected correlations and provide support for Alexander's conjecture about the non-random character of internal stresses in amorphous solids.

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## I. INTRODUCTION

Although the existence of internal stresses in glasses is well-established [1], little is known about their statistical properties and about their role in the physics of glasses and amorphous solids. Intuitively, one expects that since local stresses and strains in a glass are a by-product of the structural disorder produced by rapid freezing of a liquid (or of incompatible local packing and space-filling requirements [2] [3]), their distribution should be random. A different view is advocated in ref. [4], where it is argued that the local stresses are not random, and that their organization is closely related to the low temperature vibrational spectra of glasses. Even though the question whether internal stresses in glasses are random [5] or are subject to some complex ordering is of fundamental importance, to the best of our knowledge this issue was not directly addressed by experiments to date. A possible reason is that the effects of internal stresses are discernible only on atomic length scales, whereas on larger, but still microscopic length scales, they average to zero and the usual description of a glass as an isotropic solid with zero average internal stress, applies.

Unlike the stress singularities produced by lattice defects (vacancies, dislocations) in crystalline solids, internal stresses in glasses cannot be attributed to strongly strained core regions embedded in a weakly strained bulk. As a consequence, classical elastic theory methods for the calculation of strains and of the resultant stresses [6], are not applicable to glassy systems. The problem has been solved for periodic solids subjected to arbitrary homogeneous stress, for which one can extend the continuum approach down to atomic scales and calculate the local stress acting on a primitive cell [7]. Lately, it was shown that if the internal stresses in an amorphous solid vary sufficiently slowly on microscopic length scales, one can obtain a similar (to the crystalline case) expression for the local internal stress, with the volume of the primitive cell replaced by the Voronoi volume [4]. However, recent numerical studies of atomic stresses in two and three dimensional glassy systems at mechanical equilibrium, have demonstrated that the atomic environments

vary rapidly even between neighboring atoms at zero temperature [8, 9, 10]. The breakdown of the continuum approach implies that the macroscopic concept of stress can not be extrapolated down to atomic scales in glassy solids.

In order to bypass these difficulties, in this paper we introduce the atomic bond tension tensor that accounts for the magnitudes and the directions of the normal forces (bond tensions in the terminology of ref. [4]) acting between pairs of atoms with radial pair interaction. Since this tensor can not be identified with the stress tensor, the original question about the random vs. non-random character of the internal stresses, is replaced by that concerning the organization of atomic bond tensions in glasses.

In section II we define the atomic bond tension tensor and discuss its physical meaning. In section III we describe the measurement of this parameter in simulated two and three dimensional binary Lennard-Jones Inherent States of liquids (using the terminology of ref. [11]) and of glasses in mechanical equilibrium. In section IV we show that the local organization of bond tensions belonging to an atom is not random and that the observed correlations between the eigenvalues of the proposed tensor have a physical meaning. In section V, directional correlations and clustering are addressed, and some parallels with granular matter are drawn. These results, which demonstrate that the atomic bond tension tensor probes simulated glasses in a new way, thus extracting information unavailable by the existing methods, are discussed in section VI.

## II. THE ATOMIC BOND TENSION TENSOR

Consider a classical system of atoms with coordinates  $\{\vec{R}_i\}$ , interacting through the pair potential  $U(\{R_{ij}\})$ , where  $R_{ij} = |\vec{R}_i - \vec{R}_j|$  is the distance between atoms  $i$  and  $j$ . The tension in the "bond"  $[ij]$  between the  $i$ -th

and the  $j$ -th atom is defined as

$$J_{ij} = \frac{dU(R_{ij})}{dR_{ij}}. \quad (1)$$

Notice that in a perfect monatomic crystal, all bond tensions vanish in mechanical equilibrium, whereas in a multi-component crystal there are  $J_{ij} \neq 0$ . Non-vanishing  $J_{ij}$  are indications of “mismatches” in the bonds.

Whereas the definition of bond tensions (or, equivalently, of the normal forces) is strictly local, their distribution,  $P(J_{ij})$ , depends on the spatial order.  $P(J_{ij})$  is related to the radial distribution function  $g(r)$  by  $P(J_{ij})dJ_{ij} = g(r)dr$ , where  $P(J_{ij})dJ_{ij}$  is the probability to find bond tension with values between  $J_{ij}$  and  $J_{ij} + dJ_{ij}$ , and  $g(r)dr$  is the probability of finding a particle between  $r$  and  $r + dr$ , given a particle at the origin. Therefore, the variation in nearest neighbor separations, manifested in the width of first peak of  $g(r)$ , leads to a broad distribution of bond tensions (the distribution of the normal forces was calculated for granular materials subjected to external forces[12], [13], and for liquid and glassy systems[14]). The above connection between the distributions  $P(J_{ij})$  and  $g(r)$  has several important implications. If the separations  $R_{ij}$  between an atom and its neighbors are randomly chosen from the distribution  $g(r)$ , one does not expect to find correlations between the corresponding  $J_{ij}$ . If separations between nearest-neighbors are nearly equal, the corresponding bond tensions must be nearly equal as well (the atomic environments are either isotropically stretched or isotropically compressed).

Although there are numerous possible realizations of the set of interatomic distances  $\{R_{ij}\}$ , their number is limited by several constraints. In mechanical equilibrium, the atomic positions are constrained by the requirement that the net force on every atom in the system vanishes, i.e.,

$$\vec{f}_i = \sum_j J_{ij} \hat{R}_{ij} = 0, \quad (2)$$

where  $\hat{R}_{ij}$  is a unit vector in the direction of  $\vec{R}_{ij}$ . Moreover, mechanical stability requires that every atom in the system is located at its local energy minimum. That means that not only the Einstein frequencies of every atom in the system but also all the eigenvalues of the complete dynamic matrix are positive [4]. These requirements must be satisfied by Inherent States of a liquid (in the terminology of ref. [11]) as well as by glasses at zero temperature. In the case of granular matter thermal fluctuations play no role and only the requirement of force balance applies at rest [15], [16]. This is an important difference, especially in view of a suggestion due to Alexander [4], that the structural disorder in glasses at zero temperature should be constrained by the stability requirements.

If the distribution of bond tensions belonging to an atom  $i$  is not isotropic, the directions associated with the different bonds should be taken into consideration. This is done by introducing the tensor  $T_{ij}$  (with  $i \neq j$ ) with components

$$T_{ij}^{\alpha\beta} = J_{ij} \hat{R}_{ij}^\alpha \hat{R}_{ij}^\beta. \quad (3)$$

In order to describe the bond tensions acting on an atomic environment, the site of atom  $i$  is taken as a reference point and summation over all  $T_{ij}$  (with  $j \neq i$ ) is performed. The resulting *atomic bond tension tensor*  $\overleftrightarrow{T}_i$  is given by

$$\overleftrightarrow{T}_i = \sum_j \overleftrightarrow{T}_{ij}. \quad (4)$$

The physical meaning of  $\overleftrightarrow{T}_i$  become apparent when it is decomposed to its trace

$$J_i = \sum_j J_{ij} \quad (5)$$

and to the traceless part  $\overleftrightarrow{L}_i$ , with components

$$L_i^{\alpha\beta} = \sum_j J_{ij} \left( \hat{R}_{ij}^\alpha \hat{R}_{ij}^\beta - \frac{1}{d} \delta_{\alpha\beta} \right) \quad (6)$$

where  $d$  is the spatial dimensionality of the system and  $\delta_{\alpha\beta}$  is the Kronecker delta function. If the distribution of atomic bond tensions (ABT) is isotropic, the bond tensions acting on an atom  $i$  are completely described by the trace  $J_i$  that can be interpreted as the effective pressure acting on the atomic environment [17], [10]. The traceless tensor  $\overleftrightarrow{L}_i$ , Eq. 6, describes the effect of anisotropy on the ABT tensor. To illustrate this point, consider a monatomic crystal. At mechanical equilibrium with no external stresses, all bond tensions vanish. If the system is under hydrostatic compression, the atomic environments vary isotropically so that  $J_i \neq 0$ , while all the components  $L_i^{\alpha\beta}$  vanish. Under pure shear,  $J_i$  vanishes whereas  $L_i^{\alpha\beta} \neq 0$  and we conclude that  $\overleftrightarrow{L}_i$  describes the local effect of shear. Since  $\overleftrightarrow{L}_i$  and  $J_i$  are related to local shear and local pressure, respectively, for monatomic crystals  $T_i$  can be identified (upon suitable normalization by the surface area of the unit cell) with the local stress. For structurally disordered systems, the variation in system's volume would lead, in general, to variations in the local  $\overleftrightarrow{L}_i$ . If the system is not sheared as a whole,  $\overleftrightarrow{L}_i$  measures the weighted effect of the intrinsic anisotropy, on the distribution of ABT.

Although the ABT tensor, Eq. 4, was constructed with the aim to characterize the bond tensions acting on an atomic environment, its components are not rotation-translation invariant and, unlike bond tensions, depend on the choice of the coordinate system. In order to obtain a basis-independent (scalar) characterization of

bond tensions, one can consider the invariants of the ABT tensor (e.g., in 2 dimensions, the trace and the determinant). A drawback of such an approach is that among the  $d$  invariants ( $d$  is the dimensionality of space), only the trace, eq. 5, has the units of bond tension. An alternative approach utilizes the fact that the eigenvalues of the real symmetric matrix  $\overleftrightarrow{T}_i$  are invariant under arbitrary translation and rotation and, therefore, for every atom  $i$  in the system, there is a set of  $d$  eigenvalues  $\{t_i\} = (t_i^1, \dots, t_i^d)$  and  $d$  eigenvectors  $\{\hat{e}_i\} = (\hat{e}_i^1, \dots, \hat{e}_i^d)$  of the ABT tensor. We stress that although  $\{t_i\}$  have the same units as the components of the force acting on the atom, there is a profound difference between the two; the eigenvalues of ABT tensor are uniquely defined scalars that can be compared for different atoms at different times and external conditions (temperature, pressure). They do not vanish when the force acting on the atom vanishes, and therefore are suitable parameters to characterize atomic environments in amorphous systems and in Inherent States of liquids.

The object of the present study is to characterize the organization of atomic bond tensions in glassy systems. To do so using the ABT tensor, the distribution of the sets  $\{t_i\}$  should be known for every atom in the system. Such a distribution is trivial in monatomic crystals under hydrostatic compression, for which all the eigenvalues of ABT tensor are degenerate. While in multi-component crystalline solids the eigenvalues are, in general, non-degenerate, the fact that the atoms are arranged on a periodic lattice implies the existence of correlations between the eigenvalues. Whether the eigenvalues of the ABT tensor in structurally disordered materials are degenerate, correlated or randomly distributed, is an open question. In the following we address this question for two and three dimensional binary Lennard-Jones glasses in mechanical equilibrium.

### III. THE SIMULATED SYSTEMS

The simplest (and perhaps the only) way to calculate atomic bond tensions is by numerical simulations. Since the ABT tensor is a hitherto unexplored quantity, there are many factors to be considered when choosing the parameters of the simulated system. Local properties, such as the existence of short range structural order, or global factors, such as the dimensionality of the system[18], may affect the generality of the results. In order to suppress short-range-order effects, we use binary mixtures of two types of atoms interacting through Lennard-Jones potentials (results for monatomic systems with a pair potential that leads to local icosahedral ordering were reported elsewhere[10]). Since 2D models of glasses offer some advantages (in terms of computational load and visualization options) over the more realistic 3D systems, we consider both two and three dimensional systems with similar repulsive-attractive pair potentials.

For 3D glasses we use binary 6-12 Lennard-Jones 80 :

20 mixtures of atoms of types  $A$  and  $B$  (denoted 3DbLJ) with interaction parameters[19]:  $\varepsilon^{AA} = 1.0$ ,  $\varepsilon^{AB} = 1.5$ ,  $\varepsilon^{BB} = 0.5$ ,  $\sigma^{AA} = 1.0$ ,  $\sigma^{AB} = 0.8$ ,  $\sigma^{BB} = 0.88$ . Particles of type  $A$  are majority particles (i.e., 80%). The interaction vanishes for  $r > 2.5\sigma^{AA}$ .

For 2D glasses we use binary 6-12 Lennard-Jones 50 : 50 mixtures (denoted 2DbLJ) where[14]  $\sigma^{AB} = 0.5(\sigma^A + \sigma^B)$  for  $A, B = 1, 2$  with  $r \leq 4.5\sigma^{AB}$ . All measurements are given in reduced LJ units (for Argon these units correspond to  $\varepsilon = 120k_B$  and  $\sigma = 3.4$  Å). The bond tensions are given in units of  $\varepsilon^{AA}/\sigma^{AA}$  for the 3DbLJ systems, and  $\varepsilon/\sigma^1$  for the 2DbLJ systems. All atoms are assumed to have unit mass.

Liquids and glasses were prepared using standard molecular dynamics simulations performed at a constant volume[20]. Periodic boundary conditions were assumed. For each system type we considered two densities:  $\rho = 1.2$  and  $\rho = 1.4$  for the 3DbLJ systems, and  $\rho = 0.596$  and  $\rho = 0.735$  for the 2DbLJ systems. Such difference in densities corresponds to 5% ( 10%) difference in the average nearest neighbor separation for the 3DbLJ (2DbLJ) system. The number of atoms  $N$  for each 3DbLJ system is 16384. For 3DbLJ system with  $\rho = 1.2$ , samples with 4000 atoms were also considered. Comparison between ABT tensors calculated for the small and the large systems shows that similar results are obtained in both cases. For 2DbLJ systems, we used samples with  $N = 4096$  atoms.

Since the binary Lennard-Jones systems used in this study do not tend to crystallize [19],[14], samples at zero temperature can be prepared either by steepest descent quench from the liquid state (Inherent States of the liquid), or by obtaining a well-equilibrated glass at a sufficiently low temperature (at which all atoms are effectively trapped in their cages), and then using steepest descent quench to yield glassy systems in mechanical equilibrium. For dense 2DbLJ systems, an additional route of preparation was used: taking samples of low-density 2DbLJ glasses (at zero temperature), we decreased the length of the simulation box and rescaled all the atomic positions by 10%. Performing a steepest descent quench on the rescaled samples (in order to relax the interatomic forces) yields dense 2DbLJ systems at mechanical equilibrium. Although the above preparation routes are not equivalent, we did not find statistical differences (through comparison of means, ranges and variances) between samples prepared by different methods. Also, directional correlations related to ABT tensor are similar, regardless of the preparation method. Details about the preparation and the distribution functions  $P(\{t_i\})$  are summarized elsewhere [10].

#### IV. LOCAL ORGANIZATION OF EIGENVALUES OF ATOMIC BOND TENSION TENSOR

Since we are not aware of theoretical models that predict correlations between bond tensions in structurally disordered systems, we first address the question: Is the organization of the  $d$  eigenvalues of the ABT tensor of an atom random? If the atomic environment is such that it can be reproduced by a random choice of  $d$  numbers from the complete distribution function  $P(\{t_i\})$ , then the directional information contained in the ABT tensor is redundant. Observation of non-random organization, on the other hand, would confirm that the bond tensions acting on an atomic environment are correlated.

First we show that eigenvalues belonging to the same atom are not degenerate at zero temperature. This is an interesting point because the non-degeneracy of the  $d$  eigenvalues of ABT tensor implies that the corresponding  $d$  eigenvectors form an orthogonal basis, i.e.  $\hat{e}_i^\alpha \cdot \hat{e}_i^\beta = \delta_{\alpha\beta}$ . Since in structurally disordered systems the atomic bond tensions corresponding to any two (even nearby) atoms  $i$  and  $j$ , may be very different, one does not know a priori how to relate between the corresponding local coordinate systems  $\{\hat{e}_i\}$  and  $\{\hat{e}_j\}$ . If, however, the eigenvalues of ABT tensor are not degenerate for every atom in the system, then the local coordinate system  $\{\hat{e}_i\}$  for each atom, can be uniquely written in terms of the external global coordinate system  $\{\hat{X}_1, \dots, \hat{X}_d\}$  that we choose to project  $J_{ij}$  on. Calculation of the fraction  $f$  (in %) of pairs of eigenvalues with  $|t_i^\alpha - t_i^\beta| < \delta$  where  $\alpha \neq \beta$  ( $\alpha, \beta = 1, \dots, d$ ), yields that for  $\delta = 0.5$ ,  $f \approx 1\%$ ,  $0.2\%$  and  $2 - 3\%$  for 3DbLJ with  $\rho = 1.2$ , 3DbLJ with  $\rho = 1.4$  and 2DbLJ with  $\rho = 0.596$ , respectively. For 2DbLJ with  $\rho = 0.735$ ,  $f < 0.1\%$ . Taking  $\delta = 0.1$  yields  $f < 0.1\%$  for all systems except 2DbLJ with  $\rho = 0.596$  for which  $f \approx 0.1 - 0.15\%$ . These calculations indicate that the degeneracy increases when the density decreases. Nevertheless, the actual values of  $f$  are very small for all the systems considered, proving that the probability of degenerate pairs of eigenvalues is negligible.

Next, we compare between the distribution of the  $N$  sets  $\{t_i\}$  (for each atom  $i$  out of the  $N$  atoms in the sample) and the distribution of the  $N$  sets  $\{t_r\}$ , where the  $d$  numbers  $t_r^1, \dots, t_r^d$  are randomly chosen from the measured distribution  $P(\{t_i\})$ . For each set of  $d$  numbers, we choose two numbers according to  $t_{\min} = \min(t^1, \dots, t^d)$ ,  $t_{\max} = \max(t^1, \dots, t^d)$ , and  $(t_r)_{\min} = \min(t_r^1, \dots, t_r^d)$ ,  $(t_r)_{\max} = \max(t_r^1, \dots, t_r^d)$ , respectively[21]. Contour plots of the non-normalized distributions  $P(\{t_{\min}, t_{\max}\})$  and  $P(\{(t_r)_{\min}, (t_r)_{\max}\})$  for the systems considered (all at zero temperature) are shown in figures 1–4. The solid lines correspond to  $t_{\min} = t_{\max}$ . For the 3DbLJ glasses, each contour plot was calculated using one sample with  $N = 16384$  for every system. Similar contour plots were obtained for other samples of the system (at the same density). In

order to improve the resolution, in the case of 2DbLJ glass we considered sets with  $N = 16384$  and combined four samples for each system (we verified that  $P(\{t_1, t_2\})$  are similar in these sets). Comparing the contour plots of 3DbLJ  $\rho = 1.2$  and  $\rho = 1.4$ , and 2DbLJ  $\rho = 0.596$  and  $\rho = 0.735$  systems (figures 1.a, 2.a, 3.a and 4.a, respectively), with the contour plots of the corresponding random sets (figures 1.b, 2.b, 3.b, 4.b, respectively), we find that the distribution of eigenvalues of the ABT tensor differs from that of the random sets. In particular, the non-degeneracy of eigenvalues  $\{t_{\min}, t_{\max}\}$  is very pronounced in the simulated 3DbLJ and dense 2DbLJ glasses, but not in the corresponding random sets. We conclude that the observed non-degeneracy of eigenvalues belonging to the same atom is the consequence of a physical constraint, and not just a trivial consequence of the small probability to randomly choose  $d$  numbers with close values.

Examining the simulated and random histograms, one observes that the peak of  $P(\{t_{\min}, t_{\max}\})$  is considerably higher than the peak of  $P(\{(t_r)_{\min}, (t_r)_{\max}\})$ . The differences between the most probable "simulated" and "random" combinations of  $\{t_{\min}, t_{\max}\}$ , can be estimated by comparing the position and the height of "random" and "simulated" peaks. Those values for the systems in figures 1-4 are summarized in the table below. The fraction  $f$  of atoms with  $P(t_{\min}, t_{\max}) > 2/3h_s$ , where  $h_s$  is the height of the simulated peak, is also presented:

	peak coordinates		peak height		$f(P > 2/3h_s)$	
	simulated	random	simulated	random	simulated	random
1	(-9, 5)	(-7, 4)	100	80	0.27	0.06
2	(-50, -12)	(-44, -14)	75	50	0.24	0.003!
3	(1, 3)	(1, 1.5)	200	190	0.36	0.19
4	(-44, -32)	(-42, -40)	100	90	0.20	0.13

Comparison between the peak coordinates indicates that the most probable  $\{t_{\min}, t_{\max}\}$  are similar for the simulated and the corresponding random distributions. For the 2DbLJ and 3DbLJ with the lower densities, the corresponding  $t_{\min}$  ( $t_{\max}$ ) have small negative (positive) values, indicating that the average atomic bond tensions are small. For the dense systems, the corresponding values of  $t_{\min}$  and  $t_{\max}$  are both negative, reflecting the compression of typical atomic environments in these systems. On the other hand, comparison of the peak heights and of the fraction of atoms in the vicinity of peaks, demonstrates that the probability for the preferred combinations of  $\{t_{\min}, t_{\max}\}$  that was measured for simulated systems, can not be reconstructed by a random choice of eigenvalues.

There are also marked differences in the shapes of the distributions: the contours of  $P(\{t_{\min}, t_{\max}\})$  resemble a cone that expands towards smaller values of  $t_{\min}$ , whereas those of  $P(\{(t_r)_{\min}, (t_r)_{\max}\})$  tend to have a more circular form. To quantify the difference between the respective histograms, we calculated the Pear-

son product moment correlations

$$\rho_{X,Y} = \frac{\sum_i (X_i - \bar{X})(Y_i - \bar{Y})/n}{\sqrt{\sum_i (X_i - \bar{X})^2/n} \sqrt{\sum_i (Y_i - \bar{Y})^2/n}}$$

between  $t_{min}$  and  $t_{max}$  and between  $(t_r)_{min}$  and  $(t_r)_{max}$ . The obtained values are (with last significant digit 0.05):

<i>system</i>	$\rho(t_{min}, t_{max})$	$\rho(t_{min}^r, t_{max}^r)$
3DbLJ ( $\rho = 1.2$ )	0.7	0.3
3DbLJ ( $\rho = 1.4$ )	0.75	0.3
2DbLJ ( $\rho = 0.596$ )	0.75	0.5
2DbLJ ( $\rho = 0.735$ )	0.7	0.5

Although the shapes of the distributions (compare figures 1a and 2a for the 3d case, and figures 3a and 4a for the 2d case) and the correlations between  $t_{min}$  and  $t_{max}$  are quite similar for the densities studied, the dispersion in the values of  $t_{min}$  and  $t_{max}$  is much larger for the denser systems (notice the different scaling of the axes in the above figures).

The observed high correlations show that if  $t_{min}$  has a small (negative) value then it is highly probable that  $t_{max}$  is also small. Vice versa, if  $t_{min}$  is large we expect  $t_{max}$  to be large too. The absence of local environments with  $t_{min} \ll 0$  and  $t_{max} \gg 0$  in the simulated systems, suggests that *the local organization of the eigenvalues of ABT tensor is more isotropic than if they were randomly distributed*. On the other hand, the previously discussed observation that the eigenvalues belonging to the same atom are always non-degenerate, implies that this tendency towards local isotropy of atomic bond tension is frustrated, and that the local stresses in the glass state can not be completely characterized by isotropic pressure.

## V. DIRECTIONAL CORRELATIONS AND CLUSTERING

Having shown that the eigenvalues of ABT tensor belonging to the same atom are correlated on average, we address a related question of whether atoms with similar eigenvalues  $t_i$  are clustered in space. Since for most of the atoms the tensions in their bonds are quite small, the issue of clustering is mostly relevant for atoms with extreme (high and low) atomic bond tensions, i.e. for the tails of the distribution of  $P(t_i)$ . Using different samples of 2DbLJ and 3DbLJ glasses at zero temperature, we looked (for each sample) for clusters of atoms with  $t_{min}$  ( $t_{max}$ ) below (above) some given threshold. We did not observe clustering of atoms with high  $t_{max}$  in any of the samples. For dense 2DbLJ glass and for all 3DbLJ glasses studied, atoms with the lowest (negative) values of  $t_{min}$  were found to cluster together.

A simulated realization of a dense 2DbLJ glass in mechanical equilibrium is presented in figure 5 (both types

of atoms are drawn with the same size). The 33% of atoms with the lowest (negative) values of  $t_{min}$  are marked with yellow color and the remaining 67% are colored in blue, light blue, white, pink and red, corresponding to increasing values of  $t_{min}$ . As can be seen from the figure, the yellow atoms form nearly one dimensional percolating chains. Similar pictures were obtained for other samples. The measured percolation threshold for atoms with lowest  $t_{min}$  is  $\approx 30\%$ . This value is lower than the theoretical percolation threshold for two dimensional lattices[22]. Indeed, for randomly chosen 30% of atoms, we found considerably smaller clusters (with less atoms), that did not percolate.

Repeating the above measurements (with different thresholds) for snapshots of dense 2DbLJ glasses at higher temperatures, we did not observe such "force chains". On the other hand, running these systems at temperatures well within the vibrational regime (i.e. when no hopping occurred), and then performing a steepest descent quench to freeze the atomic positions at local energy minima (see details in [10]), we observed similar patterns. This observation suggests that the mechanical equilibrium condition of zero force on each atom is a necessary condition for the formation of percolating force chains.

To further investigate this point, a different preparation scheme was used to generate dense 2DbLJ systems. Using samples of frozen 2DbLJ glass with  $\rho = 0.596$ , all atomic positions and the length of the simulation box were rescaled by 10%, then the system was frozen again to its new local minima. Comparing between the initial (with  $\rho = 0.596$ ) and final (with  $\rho = 0.735$ ) samples, we observed that atoms with smallest  $t_{min}$  are not the same in the original and the final states. We also observed that such compression alone can not account for the formation of force chains. Only after relaxation to a state of local mechanical equilibrium, the resultant sample formed "force chains" similar to those previously described.

A percolating cluster of atoms with lowest values of  $t_{min}$  in 3DbLJ glass at zero temperature is shown in figure 6 (to improve visualization, only a single cluster is plotted). If the threshold for  $t_{min}$  is chosen to include  $\approx 5 - 6\%$  of atoms (we found that with such a threshold the system is near to or slightly above percolation), the percolating clusters form nearly one dimensional chains and loops. Although the threshold values of  $t_{min}$  are different for the compressed and non-compressed 3DbLJ glasses ( $t_{min} < -77.5$  and  $t_{min} < -23$ , respectively), we did not observe qualitative differences in the force chains.

From the observations described in the previous paragraphs, we conclude that both the mechanical equilibrium condition of zero net force on every atom and small values of  $t_{min}$ , are necessary for the formation of force chains. To see why this is so, recall that mechanical equilibrium implies that the components of the force on an atom along mutually orthogonal directions have to

vanish. In particular, for  $\alpha = 1, \dots, d$

$$f_i^\alpha = \sum_{j=1}^N J_{ij} \hat{r}_{ij} \cdot \hat{e}_i^\alpha = 0, \quad (7)$$

where  $f^\alpha$  is the component of the force acting along the eigenvector  $\hat{e}^\alpha$ . The environment of a typical atom  $i$  (corresponding to the vicinity of the peak of the distribution shown, e.g., in figure 1a) consists of mildly compressed and mildly stretched bonds, and is therefore nearly isotropic. In this case, the mechanical equilibrium condition, equation 7, can be satisfied by balancing the negative and positive tensions in the bonds of the atom with all its neighbors. Now, consider an atom with

$$(t_i)_{\min} = \min \sum_{j=1}^N J_{ij} (\hat{r}_{ij} \cdot \hat{e}_i^\alpha)^2 \ll 0.$$

that belongs to the tail of the distribution. Inspection of figure 1a reveals that for  $t_{\min} \ll 0$ , the spread of values taken by  $t_{\max}$  (and, in 3d, by the intermediate eigenvalue) increases with decreasing  $t_{\min}$  resulting in increasingly anisotropic atomic environment. In this case, the condition of zero force on atom  $i$  can only be satisfied by two similarly compressed bonds with atoms  $j$  and  $k$ , oriented at nearly opposite directions. In order to balance the forces on atom  $j$  there should be another nearest-neighbor with a highly compressed bond in a nearly opposite direction, and so on, leading to the formation of force chains. Note that above arguments imply that force chains would also be observed if one considers extremal normal forces  $J_{ij}$  instead of extremal eigenvalues of the ABT tensor  $t_i$ . This result is in accord with that of ref. [9].

The above arguments can also explain, why for two and three dimensional binary LJ glasses, similar formation of force chains of atoms with high values of  $t_{\max}$  is not likely (although in ref. [9] weaker force chains were observed for pairs of highly stretched bonds). For these systems, the eigenvalues of ABT tensor corresponding to a highly stretched atomic environment are of similar magnitude (see figures 1a, 2a, 3a and 4a) and force balance is achieved by nearly isotropic stretching of bonds between nearest neighbor atoms. Such a nearly isotropic organization implies that even if atoms with high  $t_{\max}$  were to cluster, the clusters would not take the form of nearly one-dimensional chains, but rather that of isotropic localized inclusions. These results demonstrate that the directional organization of highly stretched atomic environments is different from that of highly compressed ones. Since  $t^\alpha$  are related to the internal stresses that are present in glassy systems even in mechanical equilibrium, our numerical results agree with Alexander's conjecture about the different organization of positive and negative internal stresses in glasses (the atoms with high values of  $t_{\max}$  correspond to the "soft inclusions" discussed in ref. [4]).

## VI. DISCUSSION AND CONCLUSIONS

In this paper we defined a new parameter, the atomic bond tension (ABT) tensor, and used it to study the directional organization of atomic bond tensions. We found that in sufficiently dense systems at very low temperature, the eigenvalues  $\{t_1, \dots, t_d\}$  of ABT tensor are correlated i.e. are on the average, similar in sign and magnitude. Thus, if one observes that the environment of an atom is stretched (compressed) along some direction, one can predict with high probability that it would be compressed (stretched) along other directions as well. Based on this correlation, one may conclude that atomic environments in glasses in mechanical equilibrium are isotropic, at least in a statistical sense. However, since the eigenvalues of the ABT tensor of an atom are strictly non-degenerate, we conclude that the tendency towards perfect isotropy of atomic environments is frustrated.

Since for systems with radial pair potential there is one-to-one correspondence between the separation  $R_{ij}$  and the tension  $J_{ij}$  in the bond  $[ij]$ , the observed correlations between the bond tensions imply also correlations between the corresponding  $R_{ij}$ . Thus, various combinations of inter-atomic distances, and especially of nearest-neighbor separations in glassy systems, are constrained, and their local organization is not random. The observed deviations from randomness are associated with directional correlations; if only isotropic measures of disorder such as local volume strain [5], deviation from local sphericity [23] or local pressure [17] are considered, such correlations are not taken into account and a more random description of dense liquids and glasses results.

The results of numerical simulations reported in this paper provide a direct confirmation of Alexander's conjecture that "the reference state of the glass cannot be regarded as an arbitrary random state" (see chapter 16 in ref. [4]). Qualitatively, correlations among ABT are expected from the requirement that the forces on each atom of a structurally disordered system in mechanical equilibrium are balanced, and that each atom is caged in a potential well, i.e., that each atom is subject to a set of constraints that include zero net force and a stable atomic environment. For systems with a radial pair potential, the one-to-one correspondence between the separation of two atoms and the tension on their "bond" means that achieving balance of forces and local stability simultaneously for every atom in the system, reduces the number of degrees of freedom and sets strong constraints on the observed ABT. The observed strong correlations between the eigenvalues of ABT, in two- and three-dimensional binary LJ glasses, imply that when the asymmetry between the bonds is strong (e.g., due to two types of atoms), the directional organization of bond tensions that would comply with force balance and local stability is subject to stronger constraints.

Since the Einstein frequencies of atomic vibration around an equilibrium position are determined by the derivatives of the inter-particle pair potential, the ob-

servation of correlations between the corresponding  $R_{ij}$  implies that the atomic force constants are not random as well. Thus, further quantification of correlations in atomic force constants is required before one can incorporate them into lattice-based models which aim to reproduce the inhomogeneous network of force constants measured for simulated glasses (see, e.g., [24]).

The self-organization of normal forces under various external stresses (compression, shear) has been extensively studied for granular materials [25, 26, 27, 28], and recently also for liquids and glasses [14], and for model random packing [29]. We studied the self organization of bond tensions on an atomic level, and showed that external compression has strong qualitative effect on the local organization of the atomic bond tensions. In compressed two and three dimensional binary LJ glasses, atoms with the smallest eigenvalues of ABT tensor are organized in nearly one dimensional chains and loops. Since force chains were observed only for systems at zero temperature, we concluded that balance of forces on each atom is a necessary requirement for such organization. Although this is a customary requirement in modeling of force chains in granular materials [12], to the best of our knowledge such a requirement, although obvious, was not previously suggested in the context of glasses. In glasses with repulsive-attractive pair interactions, force balance can be achieved both by directional organization of stretched and compressed bonds in a way that their total effect is zero, or by strong,

nearly collinear compression of pairs of bonds (similar stretching of pairs of bonds is not possible, since it is not a stable configuration). For externally compressed glassy systems, there are not enough stretched bonds to balance the compressed ones, and only self-organization into one-dimensional structures (force chains) of highly compressed bonds can balance the forces for every atom.

Finally we would like to comment on several open issues for future research. We do not yet understand the physical origin of the observed conflict between the directional correlations and the strict non-degeneracy of the eigenvalues of ABT, and of the resulting frustrated tendency towards local isotropy of atomic environments in glasses. While we demonstrated the existence of organization of the atomic bond tensions in glasses and in Inherent States of liquids and quantified the extent to which they deviate from a random distribution, a more intuitive understanding of the difference between such complex organized states and purely random ones, is clearly needed.

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Zeev Olami died before this manuscript was submitted. We miss him a lot.

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### Figures

1. a. Histogram of  $P(t_{min}, t_{max})$  for 3DbLJ system with  $\rho = 1.2$  at  $T = 0$  ( $N = 16384$ ). b. Histogram  $P(t_{min}^r, t_{max}^r)$  for the same 3DbLJ system.
2. a. Histogram of  $P(t_{min}, t_{max})$  for dense 3DbLJ system with  $\rho = 1.4$  at  $T = 0$  ( $N = 16384$  particles). b. Histogram  $P(t_{min}^r, t_{max}^r)$  for the same dense 3DbLJ system.
3. a. Histogram of  $P(t_{min}, t_{max})$  for 2DbLJ systems with  $\rho = 0.596$  at  $T = 0$ . (Total number of particles is 16384.) b. Histogram  $P(t_{min}^r, t_{max}^r)$  for the same 2DbLJ systems.
4. a. Histogram of  $P(t_{min}, t_{max})$  for dense 2DbLJ systems with  $\rho = 0.735$  at  $T = 0$ . (Total number of particles is 16384.) b. Histogram  $P(t_{min}^r, t_{max}^r)$  for the same dense 2DbLJ system.
5.  $t_{min}$  for a sample of dense 2DbLJ system at zero temperature. Atoms marked in yellow are those with  $t_{min} \leq -56$  (this subset contains 33% of atoms with lowest  $t_{min}$ ).
6. 3DbLJ systems with  $\rho = 1.4$  - loop-like cluster of atoms with  $t_{min} < -77.5$ .



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